stimation of uniaxial stress component in NaCl samples compressed in a tungsten carbide anvil high-pressure x-ray apparatus

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The uniaxial stress component (USC) in NaCl samples compressed in a tungsten carbide opposed anvil high-pressure x-ray apparatus has been determined to 10 GPa by a method proposed earlier by Singh and Kennedy. In the pressure range 1–10 GPa, the pressure dependence of the lower estimates of USC can be expressed by the relation $t(p) = 0.24(\pm 0.04) + 0.11(\pm 0.005)p$, where $t(p)$ is the USC at a pressure p, $t(p)$ and p being expressed in the units of gigaPascals (GPa). These results have been used to estimate the difference, ΔP, between the pressures calculated from the hydrostatic component of strain and the strain averaged for the first six strong reflections of NaCl. ΔP is found to increase linearly from ~0.1 GPa at 1 GPa to ~0.4 GPa at 10 GPa.

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INTRODUCTION

The tungsten carbide opposed anvil x-ray cameras[1–3] ve been extensively used in the x-ray diffraction udies of solids at high pressures. The sample is aced in a small hole at the center of a boron (or boron-poxy) disk and pressed between the anvils. A collimated -ray beam is passed perpendicular to the loading di-ection and the diffraction pattern is recorded on a pho-graphic film. The data are analyzed on the assumption at the pressure on the sample is hydrostatic. In prac-e, considerable departure from the hydrostaticity of e sample pressure is caused by the facts that the sam-d is pressurized by the application of an uniaxial load d that the solids have appreciable yield strength. In h cases, the sample pressure is better described a superposition of a hydrostatic and an uniaxial stress mponent. In a previous paper,[4] a method was pro-ed to estimate the uniaxial stress component, and s successfully applied to the diffraction data for Si d NaCl. In this paper, the variation of uniaxial stress mponent in NaCl with pressure has been studied. Cl was chosen for this investigation because it is n used as a pressure-transmitting medium and as internal pressure standard in high-pressure x-ray in-stigations. A study of the variation of the uniaxial ess with pressure will be useful in evaluating the per-mance of NaCl as a pressure transmitter.

HEORY

s was shown in a previous paper,[4] the lattice strain direction (hkl) for a sample belonging to the cubic tem is given by

$$\epsilon_w(hkl) = [d_w(hkl) - d_0(hkl)]/d_0(hkl) \quad (1)$$

$$= m(p)\Gamma(hkl) + C(p), \quad (2)$$

re

$$m(p) = \alpha[S_{11}(p) - S_{12}(p) - \tfrac{1}{2}S_{44}(p)]t(p) \quad (3)$$

$$= \epsilon_w(p) + \alpha S_{12}(p)t(p) - \beta t(p)[C_{11}(p) + 4C_{12}(p) - 2C_{44}(p)]$$
$$\times\{2[C_{11}(p) + 2C_{12}(p)][C_{11}(p) - C_{12}(p) + 3C_{44}(p)]\}^{-1}, \quad (4)$$

where $\epsilon_w(p)$ is the strain corresponding to the hydrostatic component p, $t(p)$ is the uniaxial stress component, $S_{ij}(p)$ and $C_{ij}(p)$ are, respectively, the single-crystal elastic compliances and elastic moduli, and $\Gamma(hkl) = (h^2k^2 + k^2l^2 + l^2h^2)/(h^2 + k^2 + l^2)^2$. If the state of stress continuity in the crystallites is assumed, then $\alpha = 1$ and $\beta = 0$, and $\alpha = 0$ and $\beta = 1$ if the state of strain continuity is assumed. For an intermediate state $0 < \alpha, \beta > 1$.

A plot of $\epsilon_w(hkl)$ versus $\Gamma(hkl)$ is a straight line. The magnitude of $t(p)$ can be estimated from the slope of the line if $S_{ij}(p)$ are known. It must be emphasized that this method fails if either $\alpha = 0$ or $S_{11}(p) - S_{12}(p) - \frac{1}{2}S_{44}(p) = 0$. In the case of NaCl, $S_{11}(p) - S_{12}(p) - \frac{1}{2}S_{44}(p) \neq 0$, and experimentally it is found that $m(p) \neq 0$, which indicates that both α and $t(p)$ are nonzero.

III. EXPERIMENTAL WORK

The opposed anvil apparatus used in this study was similar to that described by McWhan and Bond.[3] The samples were prepared by grinding 99.9% pure NaCl from J. T. Baker Chemical Co. The powdered sample was placed in a 0.25-mm hole at the center of a boron-epoxy disk 3.2 mm in diameter and 0.5 mm thick. The boron-epoxy disk with the sample at the center was placed between the anvils such that the sample was on the axis of the anvils. The anvils were made of tungsten carbide (carboloy grade 883) and the tips were in the form of truncated cones with a 3.2-mm flat face and 85° half-cone angle. The load was applied with a Black Hawk 7-ton jack. A well-collimated beam of Mo radiati filtered by Zr foil was directed at the sample. The diffraction pattern was recorded on a cylindrical film cassette of radius 57.3 mm. The diffraction patterns were occasionally recorded on a two-film cassette[5] to cross-check the results. For each sample the diffraction pattern was recorded with the sample under pressure; a second pattern was recorded after releasing th pressure to 1 atm. A fresh boron-epoxy disk was used after each run. After each run, the centering of the sample was checked under a microscope. The displace ment of the sample after application of pressure was observed quite infrequently; only two out of a total of 1

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TABLE I. The various parameters derived from the measurement of lattice parameters of NaCl at high pressure. S_ϵ, S_m, and S_c denote, respectively, the standard deviations of ϵ, m, and C.

Run	$m(p)\times10^2$	$-C(p)\times10^2$	$S_\epsilon\times10^2$	$S_m\times10^2$	$S_c\times10^2$	$\epsilon_w(p)\times10^2$	$-t(p)$ (GPa)[a]
A-10	0.788	3.325	0.11	0.34	0.07	3.409	0.375
B-6	0.217	1.138	0.09	0.29	0.06	1.185	0.135
B-9	0.590	1.738	0.11	0.35	0.07	1.839	0.331
B-14	0.654	3.414	0.11	0.35	0.07	3.482	0.309
B-19	1.042	4.636	0.19	0.61	0.12	4.716	0.464
C-12	0.411	2.909	0.08	0.25	0.05	2.958	0.202
D-10	0.607	2.085	0.07	0.21	0.04	2.178	0.325
D-15	0.474	3.446	0.10	0.32	0.06	3.495	0.224
D-20	0.202	3.668	0.11	0.35	0.07	3.688	0.094
E-10	0.353	1.880	0.09	0.30	0.06	1.938	0.194
G-25	0.833	5.861	0.11	0.35	0.07	5.912	0.361
H-30	0.480	6.984	0.12	0.38	0.08	7.006	0.210
I-25	0.432	5.707	0.14	0.45	0.09	5.735	0.188
J-30	0.900	7.409	0.16	0.50	0.10	7.449	0.396
K-10	0.393	2.044	0.06	0.18	0.04	2.105	0.211
L-30	0.758	6.402	0.13	0.40	0.09	6.444	0.340
M-20	1.199	4.306	0.13	0.43	0.09	4.404	0.540

[a]Negative sign indicates that $t(p)$ is compressive.

runs showed sample displacement in excess of 0.02 mm, and were discarded. The exposure time with a Machlett x-ray tube operated at 45 kV and 18 MA ranged from 6 h for low sample pressures to 12 h for the high (~10 GPa) sample pressures. In the entire pressure range (~1—10 GPa) it was possible to record 200, 220, 222, 400, 420, and 422 reflections.

IV. RESULTS AND DISCUSSIONS

The lattice strains $\epsilon_w(hkl)$ for 200, 220, 222, 400, 420, and 422 reflections were calculated from the measurements on the patterns recorded with the sample at high pressure and the corresponding patterns taken with the sample at atmospheric pressure. Equation (2) was fitted to the $\epsilon_w(hkl)$ data by the method of least squares. The slope $m(p)$, and the intercept on the $\epsilon_w(hkl)$ axis, $C(p)$, obtained from 17 different runs are listed in Table I. A plot of $m(p)$ against $C(p)$, and also p, is shown in Fig. 1.

The estimates of $t(p)$ can be made from the knowledge of $S_{ij}(p)$ and $m(p)$. To calculate $S_{ij}(p)$ at a given pressure p, first $C_{11}(p)$, $C_{12}(p)$, and $C_{44}(p)$ were evaluated using the values of $\partial C_{11}/\partial p$, $\partial C_{12}/\partial p$, and $\partial C_{44}/\partial p$ obtained by Bartels and Schuele.[6] $S_{11}(p)$, $S_{12}(p)$, and $S_{44}(p)$ were then calculated by using the well-known relations among the elastic compliances and the elastic moduli. It must be mentioned that only the first derivatives of the elastic moduli were used in the evaluation of $S_{ij}(p)$. The values of $S_{ij}(p)$, especially in the high-pressure range, might be in error because of the neglect of the higher-order pressure derivatives of the elastic moduli. In a recent study, Spetzler, Sammis, and O'Connell[7] reported the second derivatives of the various elastic moduli of NaCl. However, their data suggest maxima in the C_{ij}^S-vs-p curves occurring at 7.4, 4.8, and 4.1 GPa, respectively, for C_{11}^S, C_{12}^S, and C_{44}^S. Above these pressures the elastic moduli decrease with increasing pressure. A maximum in the C_{ij}^S-vs-p curve is expected since the first and the second derivatives of C_{ij} have opposite signs. However, occurrence of maxima at rather low pressures indicates that either the values of the second derivatives are too large due to experimental errors or the third and higher derivatives become appreciable above ~4 GPa. Because of this uncertainty the results of Spetzler, Sammis, and O'Connell[7] were not used in the present case. Using values of $S_{ij}(p)$ estimated from the data of Bartels and Schuele,[6] the lower estimates of $t(p)$ were obtained. From the knowledge of $S_{12}(p)$ and $t(p)$, $\epsilon_w(p)$ values were calculated for each run using relation (4) with $\beta=0$ and $\alpha=1$. The values of $t(p)$ and $\epsilon_w(p)$ for each run are listed in Table I. A plot of $t(p)$ versus p is shown in Fig. 2. The pressure derivative of $t(p)$ was determined by fitting an equation of the form

$$t(p)=t(0)+t'(0)p$$

by the method of least squares. The values of $t(0)$ and $t'(0)$ were found to be, respectively, 0.24 ± 0.04 GPa and 0.011 ± 0.005, the errors indicated being the probable errors.

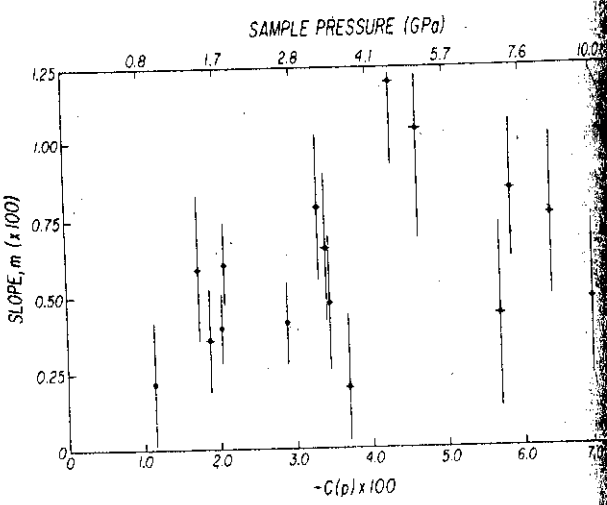
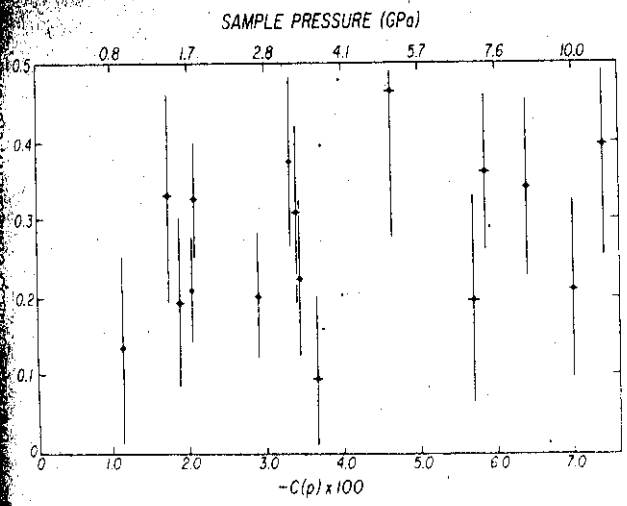


FIG. 1. The slope of the $\epsilon_w(hkl)$-vs-$\Gamma(hkl)$ line as a function of pressure.



IG. 2. The variation of the uniaxial stress component with ressure. The uniaxial stress component is calculated with =1.

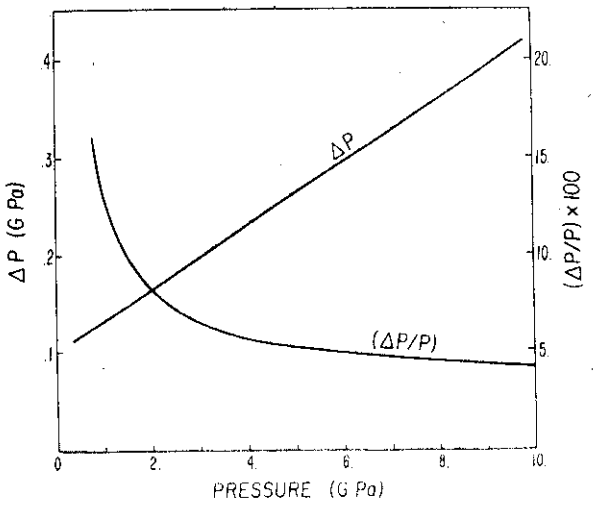


FIG. 3. ΔP and $\Delta P/P$ as a function of P. ΔP is the difference between the pressure calculated from $\epsilon(p)$ and $\bar{\epsilon}(hkl)$.

The x-ray diffraction experiments have been done refully to minimize the various errors, and the x-ray ta are of highest quality that can be obtained from ch an experimental setup. In deriving $m(p)$ from plots ch as that shown in Fig. 1, we are making use of all differences in strains which depend on (hkl). This ads to a large scatter in the determination of $m(p)$. In e following paragraphs a brief discussion of the errors measurement is given.

The random errors in the measurement arise mainly om the errors in reading the film. An analysis of the ta indicates a standard deviation of 0.03 mm in the asurement of the diffraction ring diameters. This ounts to a standard deviation of 0.007° in the deter- ination of θ angles. The standard deviation in the de- rmination of strains, ϵ, is angle dependent and ranges om 0.001 for (200) reflection to 0.0003 for (422) flection.

The departures of the actual experimental condition om the ideal Debye-Scherrer geometry lead to system- ic errors.[8] These errors are dependent on the θ angle. the present case, the most important source of error the displacement of the sample from the center of the vil face. As stated earlier, the runs showing a sample ift of more than 0.02 mm were discarded. The es- mated error in the θ angle is less than 0.005°. The sorption error is small for NaCl when Mo radiation used. It must be emphasized that all the systematic rors are functions of θ, and since there is no correla- n between $\Gamma(hkl)$ and θ, these systematic errors will pear as random errors in a $\epsilon(hkl)$-vs-$\Gamma(hkl)$ plot. The ndard deviations listed in Table I are derived from e least-squares fit of the $\epsilon(hkl)$-vs-$\Gamma(hkl)$ plot, and erefore include both the random and the θ-dependent stematic errors. In deriving $t(p)$ from the $m(p)$ values, (p) values are needed. Any error in $S_{ij}(p)$ values will d to a systematic error in $t(p)$. The error from this rce alone is nearly 1%, and is negligible as com- ed to the errors of measurement.

Recently, Kinsland and Bassett[9] attempted to measure the USC in NaCl and MgO by measuring the ellipticity of the x-ray diffraction rings[10] in a diamond cell. These measurements indicate the presence of large USC in MgO, but not in NaCl. Most probably the ellipticity in the diffraction rings caused by USC in NaCl is smaller than the error in their experiments.[9]

The uniaxial stress component is essentially the difference between the axial and the radial stress components. From simple arguments[4,11] it can be shown that the difference between the axial and the radial stress components is equal to the flow stress of the sample material. The flow stress of a material is very sensitive to the grain size and the strain history of the sample. As a result, the USC also will depend on the grain size and the strain history of the sample. Often, the USC measured on two batches of samples differed greatly. For example, in a previous study[4] a value of 0.55 GPa was obtained for USC at $C(p) = 0.01$. In the present set of measurements an average value of 0.25 GPa is obtained. The present set of measurements were made on the specimen from a single batch of powdered NaCl. The average grain size was 0.02 mm. However, the effect of the grain size and the strain history on USC is prominent only at low pressures. At high pressures the deformation of the sample is severe, and produces a grain structure which is nearly independent of the initial grain size.

The strain $\epsilon(hkl)$ as calculated from Eq. (1) is less than the hydrostatic component $\epsilon(p)$, since $\epsilon(hkl)$ and $\epsilon(p)$ are negative while the term containing $t(p)$ in Eq. (2) is positive. NaCl is often used as a pressure standard. The pressure is calculated from the knowledge of the equation of state of NaCl and the lattice strain averaged over all the observed reflections. The average lattice strain $\bar{\epsilon}(hkl)$ is given by

$$\bar{\epsilon}(hkl) = \epsilon(p) + S_{12}(p)t(p) + [S_{11}(p) - S_{12}(p) - \tfrac{1}{2}S_{44}(p)]t(p)\bar{\Gamma}(hkl).$$

$\bar{\Gamma}(hkl)$ is the average of $\Gamma(hkl)$ for the line used in the calculation of $\bar{\epsilon}(hkl)$. In practice, 200, 220, 400, 420, and 422 lines are easily observed. $\bar{\Gamma}(hkl)$ for these lines is 0.1656. The difference, ΔP, between the pressure calculated from $\epsilon(p)$ and the pressure calculated from $\bar{\epsilon}(hkl)$ has been estimated using Decker's equation of state,[12] and is shown in Fig. 3. It is seen that ΔP increases almost linearly from ~0.1 GPa at 1 GPa to ~0.4 GPa at 10 GPa.

The results reported here correspond to a tungsten carbide opposed anvil setup, a boron-epoxy gasket of the dimensions stated earlier, and an initial average grain size of 0.02 mm of the sample material. It can be easily shown[4,11] that the USC is equal to the flow stress of the sample material, and therefore should depend only on the grain size and the pressure of the sample. Thus, one would expect the magnitude of USC to be independent of the experimental parameters, such as the dimensions of the anvil faces and of the boron-epoxy gasket. Further, the experiments with ungasketed opposed anvil devices[9,10] should also give results in agreement with the results from gasketed experiments. However, until more extensive measurements with different size gaskets and also with ungasketed apparatus are available to support this point, it is desirable to bear in mind the experimental conditions under which these results are obtained.

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